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Final Program Report to ONR

Synthesis of PVDF Homo- and Co-polymers with Well-defined Molecular Structure; Using Borane/Oxygen Coordination Free Radical Initiator

Principle Investigator: T. C. (Mike) Chung
Contract/Grant Number: N00014-99-1-0443

Summary:

Several important progresses have been made in the past three-year ONR program. (i) We have developed a new polymer chemistry that allows the polymerization of fluoro-monomers in bulk condition at ambient temperature. (ii) A new family of ferroelectric polymorphs fluoro-terpolymers have been prepared, which comprise vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a chloro-containing third monomer, including vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), chlorotrifluoroethylene (CTFE). The new terpolymers show narrow molecular weight and composition distributions and good processibility. (iii) The terpolymers exhibit excellent electric properties. Comparing with the known VDF/TrFE copolymer, the slightly bulky chlorine atoms randomly distributed along the polymer chain spontaneously alter the crystalline phase from β -phase (all-trans conformation) to γ -phase (tttg⁺tttg⁻ conformation), without significant reduction of overall crystallinity. The Curie (F-P) transition from γ -phase to α -phase (tg⁺tg⁻ conformation) occurs at near ambient temperature, with a very small activation energy and slim hysteresis loop during heating and cooling cycle. The terpolymers show high dielectric constant (>50) and large electrostrictive response (~5%) at ambient temperature, and exhibiting common ferroelectric relaxor behaviors with a broad dielectric peak that shifted toward higher temperatures as the frequency increased, and a slim polarization hysteresis loop at near the dielectric peak (around ambient temperature).

Objectives:

Strong interest has been generated in recent decades regarding the development of ferroelectric materials with high performance for such applications as electromechanical transducers, actuators, and sensors. Traditional electroactive materials (piezoceramic and magnetostrictive materials) have been found to suffer from low strain response (<1%), despite their high dielectric constant, low hysteresis, and fast speed. Developing new ferroelectric materials with high strain, high elastic density, and high electromechanical coupling has been a scientific and technological challenge. Comparing to current ceramic-based materials, polymeric materials could offer many unique features, such as light weight, low cost, easy processability into thin and flexible films of various shapes and sizes, large strain without structure fatigue, and most importantly, flexible property-structure design via molecular tailoring.

Despite many potential advantages, the progress in developing ferroelectric polymer has been very slow. Most polymers have the disadvantages of low electric field sensitivity in terms of their dielectric constant, piezoelectric coefficient, and electromechanical coupling coefficient, which limit their use in electroactive applications. In the past decade, most research activities in ferroelectric polymers have been focused on ferroelectric fluorocarbon polymers, especially

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semicrystalline polyvinylidene difluoride (PVDF) and poly(vinylidene difluoride-co-trifluoroethylene) (VDF/TrFE) copolymers, due to strong dipole in C-F bonds.

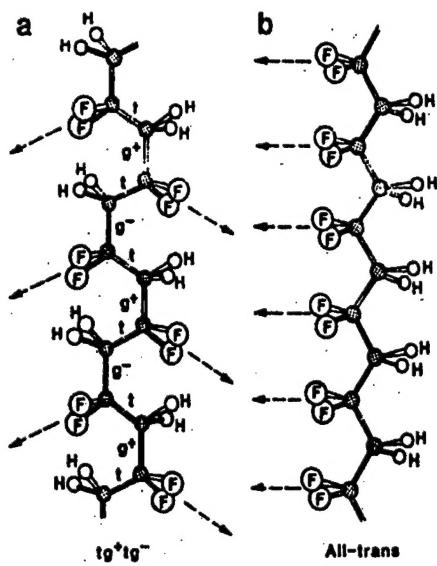


Figure 1. Schematic depiction of the two most common chain conformations in PVDF : (a) tg^+tg^- in α -phase and (b) all-trans in β -phase.

In 1969, the discovery of the enhancement of piezoelectric activity in PVDF by Kawai led to the revelation of ferroelectricity properties. The polymer chains are usually crystallized into a (non-polar) α -phase with tg^+tg^- chain conformations (Figure 1) whose dipole components normal to the chain are antiparallel and neutral to each other. It is necessary that polymer film be subjected to mechanical stretching and electrical poling to get the (ferroelectric) β -phase with the extended planar zigzag (*all-trans*) conformation. It was speculative to say how much improvement of the dielectric and piezoelectric properties might yet be achieved by modification of the chemical

structure of the polymer, especially through the spontaneous formation of the desirable ferroelectric phase by simple crystallization from the melt.

The most successful example is in the VDF/TrFE copolymers. The randomly distributed VDF and TrFE units in the VDF/TrFE copolymer form the co-crystalline phase (Figure 2) in the whole composition range of the copolymers. The greater proportion of bulky trifluorine atoms in TrFE units prevents the polymer chains from accommodating the tg^+tg^- conformation. Therefore, copolymers crystallized at room temperature into a ferroelectric phase with an extended planar zigzag (*all-trans*) conformation, whose crystalline phase is similar to the ferroelectric β -phase of PVDF homopolymer.

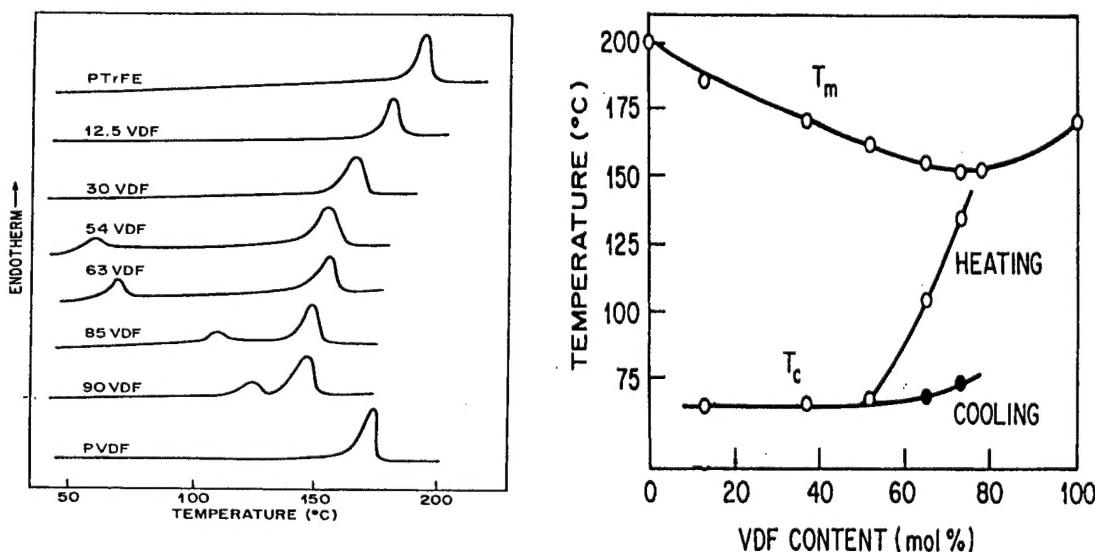


Figure 2. Thermal transitions of VDF/TrFE copolymers with various VDF contents.

Probably the most solid evidence for ferroelectricity in the VDF/TrFE copolymer is the existence of the F-P phase transition or Curie temperature (T_c), which represents the first time this effect has been observed in a synthetic polymer. The lowest Curie temperature of the copolymer is about 65°C in the composition VDF/TrFE=55/45 mole ratio.

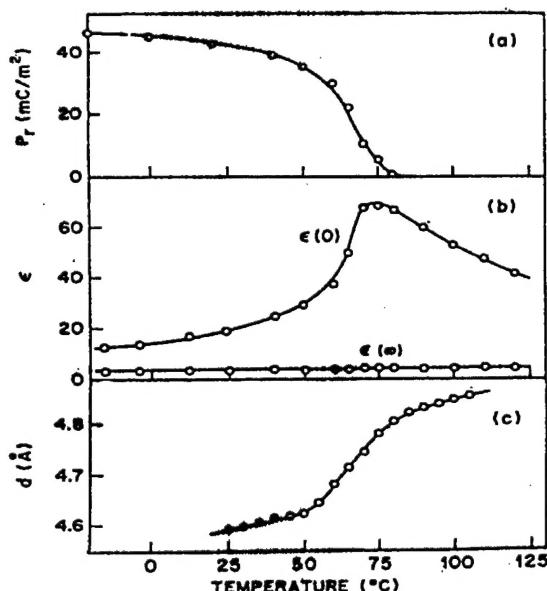


Figure 3. Temperature dependence of remnant polarization (P_r), dielectric constant (ϵ), and lattice spacing (d) for VDF/TrFE= 55/45 copolymer.

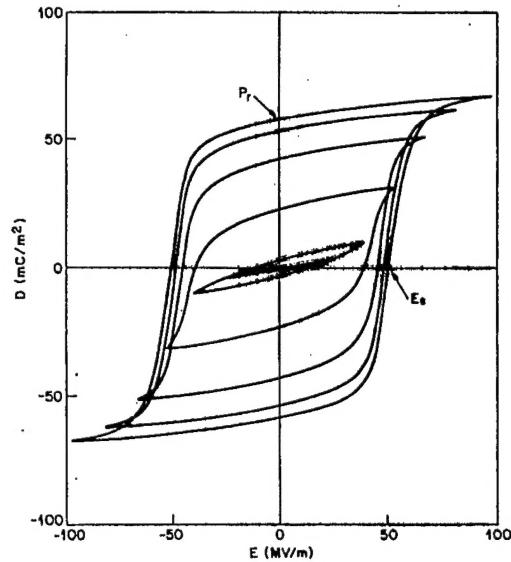


Figure 4. The D-E hysteresis loops of VDF/TrFE=55/45 copolymer at various electric fields.

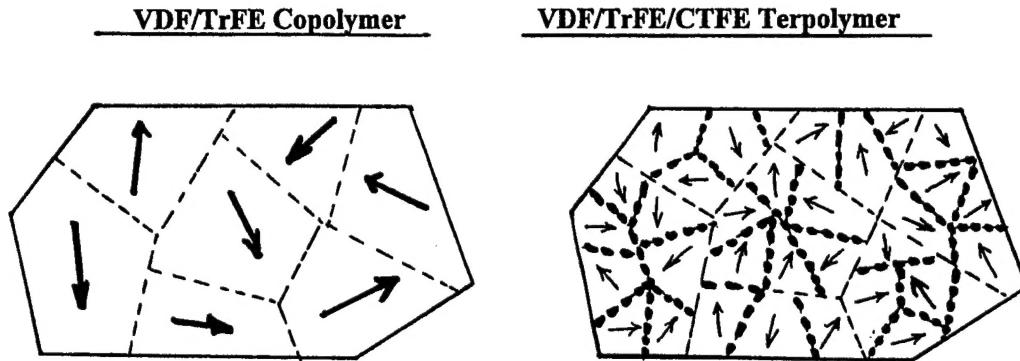
As shown in Figure 3, at near the Curie transition temperature, the dielectric constant (ϵ) shows a maximum, the electric polarization (P_r) decreases to zero, and the lattice spacing changes. Due to the high Curie (F-P) transition temperature, the response of the dipoles to the electric field is very low at ambient temperature. The slow response to the electric field is also revealed in a large polarization hysteresis loop (Figure 4), due to the high energy barrier of switching the dipole direction at ambient temperature.

Many projects have been devoted to the general goal of reducing the F-P transition temperature and generating large electric-induced mechanical response at ambient temperature. The direct correlation between the reduced polar domain size and lower energy barrier, shown in ferroelectric ceramic materials, led to many attempts to alter copolymer morphology, such as by melt-quenching or by electron-irradiation to break crystalline domains, which improved some electric responses, but was also accompanied by many side reactions and limitations.

Approach:

In our ONR program, we have adopted a new chemical strategy of altering crystalline domains and creating relaxor ferroelectric behavior of VDF/TrFE copolymer, with the objective of achieving a processable polymer with controlled phase transition temperature, high dielectric constant, and fast and large electromechanical response at ambient temperature. The research approach was to homogeneously incorporate a small amount of bulky ter-monomer units, such as

vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), chlorotrifluoroethylene (CTFE), as the crystalline defects into a VDF/TrFE copolymer chain. Ideally, the incorporated ter-monomers result in a reduced polar domain size without changing the overall crystallinity, as illustrated below.



The smaller polar domains reduce the energy barrier needed in F-P phase transition, and therefore reduces the Curie transition temperature and its activation energy. The low energy phase transition (polar-nonpolar) at ambient temperature will translate to small polarization hysteresis and large electric-induced strain. In the terpolymer preparation, it is essential to develop a new chemistry that can obtain the terpolymer with high molecular weight, narrow molecular weight and composition distributions. The conventional emulsion and suspension processes in current fluoropolymer synthesis would be very difficult to maintain constant monomer feed ratio in aqueous solution.

Progress:

Some important progresses have been made in this three-year ONR program, including (i) a new polymer chemistry to prepare fluoropolymers, (ii) a new family of ferroelectric polymorphs terpolymers comprising vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a chloro-containing third monomer, including vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), chlorotrifluoroethylene (CTFE), with good processibility and narrow molecular weight and composition distributions, and (iii) the terpolymers exhibiting excellent electric properties with high dielectric constant, slim polarization hysteresis loop, and large electrostrictive response (~5%) at ambient temperature. The detailed experiemntal results are discussed below:

(1) New Polymer Chemistry Based on Borane/Oxygen Adducts

The following Equation illustrates the bulk polymerization mechansim initiated by the oxidation adducts of the organoborane molecule at ambient temperature. Upon exposure to a controlled quantity of oxygen, asymmetrical alkylborane (I) is selectively autoxidized at the linear alkyl group to produce ethylperoxylborane (II). The peroxyborane (II) behaves very differently from regular benzoyl peroxides and consequently decomposes to an alkoxy radical (C-O[•]) and a borinate radical (B-O[•]) (III) that is relatively stable due to the back-donating of electron density to the empty p-orbital of boron. In the presence of fluro-monomers, the homolytical cleavage of peroxide occurs even at very low temperatures (-30° C). The alkoxy

radical is very reactive and initiates the radical polymerization at ambient temperature. On the other hand, the borinate radical forms a weak and reversible bond with the growing chain end, which assures the "stable" radical polymerization. During the propagating reaction, a coordination intermediate (IV) may form due to the B-F acid-base complex between the active site and the incoming monomer. Such an interaction will regulate the insertion of monomers in a preferred head-to-tail sequence.

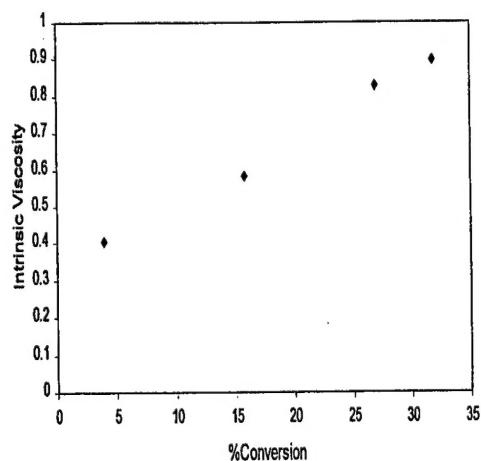
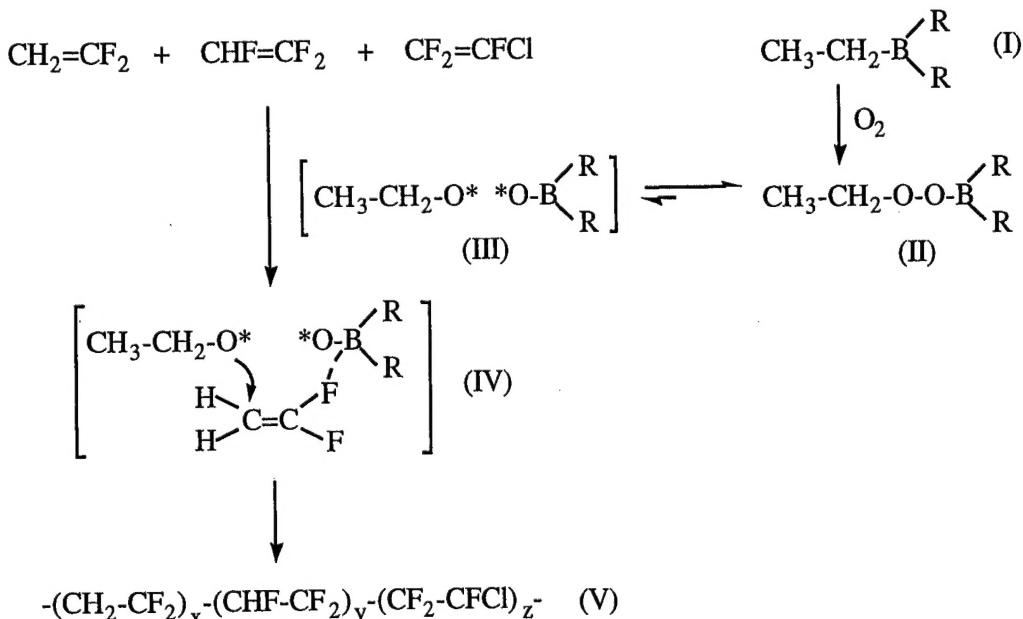


Figure 5. Intrinsic viscosity of VDF/TrFE/CTFE terpolymer vs. monomer conversion.

No chain transfer and termination reactions were observed during the propagating process, which leads to polymer with relatively narrow molecular weight and composition distributions. Figure 5 shows that the VDF/TrFE/CTFE terpolymer^{30,31} increases its molecular weight with the conversion of monomers. It is interesting to note that this chemistry also produces terpolymer with very few impurities (boric acid and butanol) that can be easily removed by methanol.

(ii) A New Family of Ferroelectric Polymorphs Terpolymers

As illustrated in the following Scheme, several chloro-containing ter-monomers, including vinyl chloride (VC), 1,1-chlorofluoroethylene (CFE), 1-chloro-2,2-difluoroethylene (CDFE), chlorotrifluoroethylene (CTFE), were copolymerized with VDF and TrFE to form terpolymers, with narrow molecular weight and composition distributions. For comparison, two reference terpolymers containing a smaller size vinyl fluoride (VF) and a larger size hexafluoropropylene (HFP) units, respectively, were also prepared.

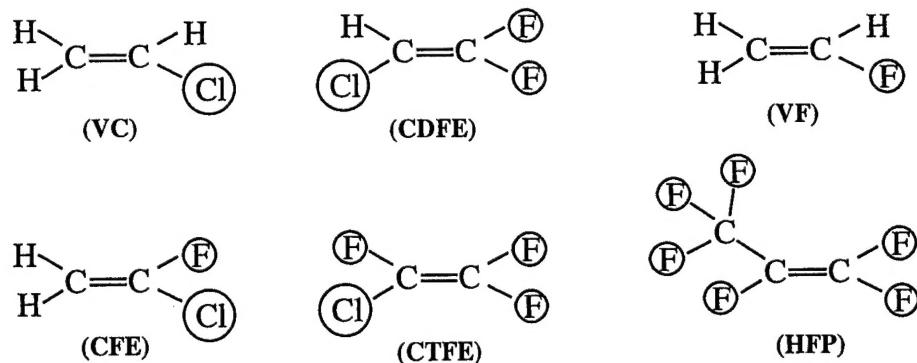


Table 1 summarizes several VDF/TrFE/CTFE terpolymers prepared by the same method. All terpolymers are high molecular weight (>20,000 g/mole) polymers with a good solubility in common organic solvents and melt processable at >150° C.

Table 1. A summary of VDF/TrFE/CTFE terpolymers prepared by borane/oxygen initiator and bulk process

Sample No.	Terpolymer mole ratio			Melting temperature		Phase transition temperature		[η] (MEK) (35°C)
	VDF	TrFE	CTFE	T _m (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)	
1	72.2	17.8	10.0	107.8	17.8	25.0	0.4	0.38
2	66.0	22.5	11.5	117.2	21.6	25.2	2.5	0.42
3	66.1	21.4	12.5	115.6	20.5	25.8	1.8	0.42
4	63.1	25.4	11.5	113.7	18.5	none	none	0.49
5	61.4	25.3	13.3	111.3	17.8	15.6	1.5	0.69
6	58.0	33.1	8.9	130.0	21.3	31.6	2.5	0.63
7	60.0	36.0	4.0	140.9	25.7	43.8	6.5	0.58
8	55.6	36.1	8.3	124.6	21.2	none	none	0.54
9*	60.0	35.1	6.9	126.6	20.9	33.5	1.6	0.78
10*	59.3	32.9	7.8	125.1	20.3	24.8	1.4	0.80
11*	57.3	31.2	11.5	111.1	14.8	None	None	0.75

- Control monomer feed ratio during the polymerization.
- MEK: methyl ethyl ketone. none: no observable.

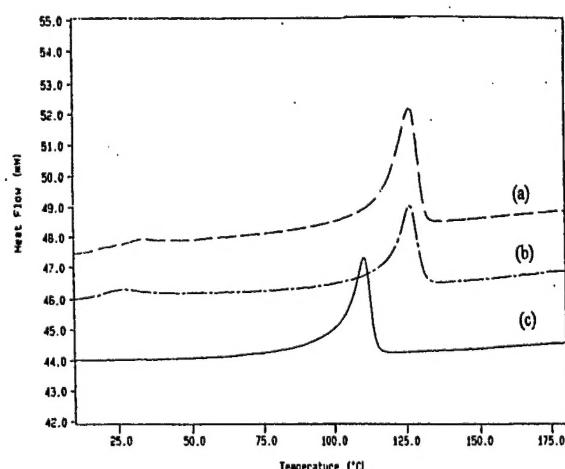


Figure 6. DSC comparison of three VDF/TrFE/CTFE terpolymers (a) sample 9, (b) sample 10, and (c) sample 11 in Table 1.

Despite having relatively high CTFE contents, all the terpolymers are still semicrystalline thermoplastics with melting temperatures >100° C, and $\Delta H > 17$ J/g. Figure 6 compares the DSC curves of three VDF/TrFE/CTFE terpolymers (samples 9, 10, and 11). The relatively well-defined melting and Curie transition temperatures imply a relatively uniform molecular structure.

Apparently, the CTFE units serve as a defect (by introducing a gauche bond) to prevent the extension of crystallization, which results in the reduction of the lamella thickness of the crystal. In general, the third CTFE monomer units in VDF/TrFE/CTFE terpolymers shift (and broaden) the Curie temperature to lower, at near ambient temperature for samples 1, 2, 3, and 10, and almost eliminate the transition for samples 4, 8, and 11. That indicates a very small energy barrier in the phase transition and implies a smaller crystalline domain. The results are consistent with the electric responses of the terpolymer under an electric field.

(3) Electric Properties of Terpolymers

Figures 7 shows the dielectric constant of 59.3/32.9/7.8 in the VDF/TrFE/CTFE terpolymer (sample 10) and 57.3/31.2/11.5 in the VDF/TrFE/CTFE terpolymer (sample 11) during the heating-cooling cycles. Gold (<1 μm thickness) was sputtered on both surfaces of the polymer film ($\sim 30 \mu\text{m}$ thickness).

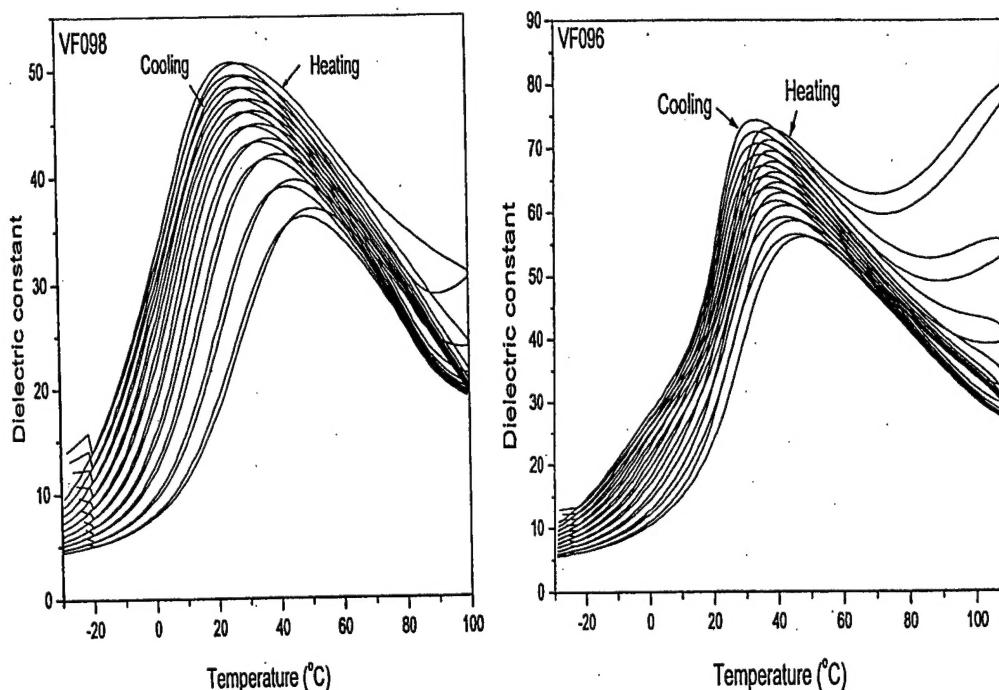


Figure 7. Temperature dependence of dielectric constant in two terpolymers, (right) sample 10 and (left) sample 11 during heating-cooling cycles. The frequencies from top to bottom of the dielectric curve range from 1 kHz to 300 kHz.

In general, the dielectric constant hysteresis during the heating-cooling cycles is very small, and the dielectric peak appears near the ambient temperature, which is well below the dielectric peak observed in VDF/TrFE=55/45 copolymer ($\sim 65^\circ \text{C}$) with a large hysteresis loop. Diffuse dielectric peaks and peaks shifting toward higher temperatures as the frequency increases are common features of relaxor ferroelectrics.

Table 2 summarizes the dielectric constants of the terpolymers, which were estimated from the heating cycles. Most of the terpolymers show high dielectric constants at ambient temperature. Samples 4 and 5 exhibit dielectric constants as high as 53.5 and 53.1 (1 kHz),

respectively, at 22° C. In addition, the mechanical stretching of the polymer film, usually very important for increasing the dielectric constant in VDF/TrFE copolymers, is not necessary in these terpolymers. The effective orientation of dipoles under an electric field may be attributed to the low phase transition energy, which occurs at near ambient temperature.

Table 2. A summary of electric properties for the VDF/TrFE/CTFE terpolymers shown in Table 1.

Samples No.	P _{max} (mC/m ²)	E _c (MV/m)	Dielectric constant*	Dielectric loss
100 MV/m, 10 Hz, 22° C				1 KHz, 22° C
1	82	19.6	27.0	0.04
2	78	24.1	22.4	0.03
3	-	-	40.9	0.04
4	76	19.8	53.5	0.06
5	75	33.7	53.1	0.06
6	63	16.4	33.0	0.05
7	87	21.8	26.4	0.04
8	36	7.6	42.4	0.07
9	110	55.9	52.7	0.07
10	70	11.5	51.0	0.07
11	45	39.4	50.5	0.06

* based on heating cycle

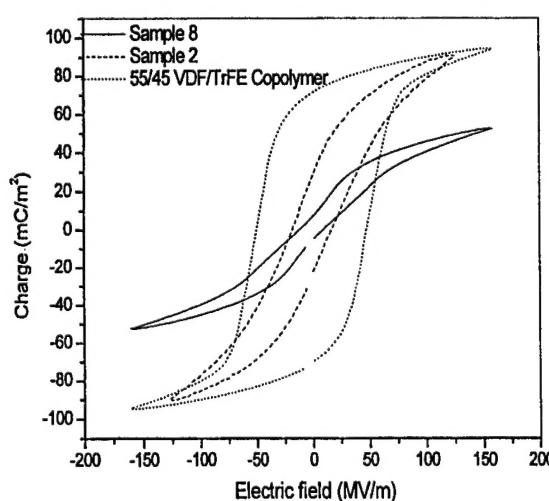


Figure 8. The comparison of polarization hysteresis loops between two VDF/TrFE/CTFE terpolymers (samples 2 and 8) and a VDF/TrFE (55/45) copolymer.

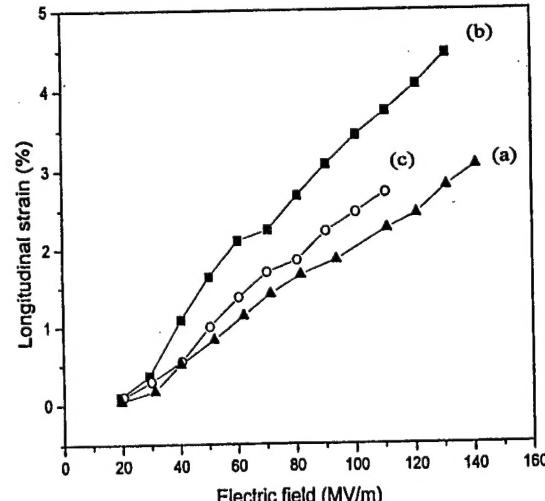


Figure 9. Electric field induced strain under electric field measured at electric field from 0-150 MV/m of three VDF/TrFE/CTFE terpolymers, samples 9 (a), 10 (b), and 11 (c).

The polarization hysteresis loop was measured by a Sawyer-Tower circuit with a frequency range between 1 and 10 Hz. Figure 8 compares the polarization hysteresis loops of two terpolymers (samples 2 and 8) and a VDF/TrFE=55/45 copolymer. Both terpolymers show significantly smaller hysteresis than the copolymer (55/45) that has the narrowest polarization

hysteresis loop observed in the copolymer samples. Sample 2 (with VDF/TrFE/CTFE = 66/22.5/11.5 mole ratio) still maintains a high polarization level ($P_{max} = 78 \text{ mC/m}^2$ at $E=100\text{MV/m}$) with reduced coercive field (17.3 MV/m at $P=0$) and remanent polarization (25.2 mC/m^2 at $E=0$). Sample 8 (with VDF/TrFE/CTFE = 55.6/36.1/8.3 mole ratio) exhibits a very slim loop with very small coercive field and remanent polarization, as well as an overall reduced polarization level. These results indicate that the VDF/TrFE crystalline defects introduced by the incorporated CTFE termonomer units cannot be recovered by the application of a high electric field. It is interesting to note that the polarization hysteresis loop of sample 8 gradually appeared with reduced temperatures ($<0^\circ \text{C}$), another feature common to all relaxor ferroelectrics.

The electric field-induced strain was measured at ambient temperature in the field range of 0-150 MV/m using a bimorph-based strain sensor, which consists of a piezoelectric bimorph-based cantilever dilatometer. Figure 9 shows three samples 9, 10, and 11, having VDF/TrFE/CTFE mole ratios of 60.0/35.1/6.9, 59.3/32.9/7.8, and 57.3/31.2/11.5, respectively. At ambient temperature, the longitudinal strain reached about 4.5% for sample 10 under an electric field of 130 MV/m. A nearly straight line of S vs. P^2 for sample 10 indicates the electrostrictive response in the VDF/TrFE/CTFE terpolymer. Based on the electrostrictive relationship $S=QP^2$, this equation yields an electrostrictive coefficient (Q) of about $-5.57 \text{ m}^4/\text{C}^2$. Progress:

Papers and Patent Resulting From This Award

1. "Semicrystalline Ferroelectric Fluoropolymers and Process for preparing Same" T. C. Chung and A. Petchsuk, U. S. Patent (allowed).
2. "Synthesis and Electric Property of VDF/TrFE/HFP Terpolymers" A. Petchsuk, and T. C. Chung, Mat. Res. Soc. Sym. Proc. 600, 53, 2000.
3. "Ferroelectric Polymers with Large Electrostriction; Based on Semicrystalline VDF/TrFE/CTFE Terpolymers" T. C. Chung and A. Petchsuk, Ferroelectrics Lett. 28, 3/4, 2001.
4. "Ferroelectric VDF/TrFE/CTFE Terpolymers; Synthesis and Electric Properties" T. C. Chung and A. Petchsuk, SPIE Proc. 4328, 117, 2001
5. "Polymers, Ferroelectric" T. C. Chung, Encyclopedia of Physical Science and Technologys. 3rd Ed. (in press).
6. "Synthesis of Syndiotactic Polystyrene (s-PS) Containing a Terminal Polar Group and Diblock Copolymers Containing s-PS and Polar Polymers" G. Xu and T. C. Chung, Macromolecules, 32, 8689, 1999.
7. "Synthesis of Syndiotactic Polystyrene Derivatives Containing Amino Groups" G. Xu and T. C. Chung, Macromolecules, 33, 5803, 2000.
8. "A Novel Consecutive Chain Transfer Reaction to p-Methylstyrene and Hydrogen During Metallocene-mediated Olefin Polymerization, T. C. Chung and J. Y. Dong" J. Am. Chem. Soc. 123, 4871, 2001.
9. "Synthesis of Functional Polyolefin Copolymers with Graft and Block Structures, T. C. Chung, Prog. Polym. Sci. 27, 39, 2002.
10. A New Living Free Radical Initiator; Alkylperoxy-9-borafluorene, T. C. Chung and G. Xu, J. Am. Chem. Soc. (pending).